

# COAL THERMOLYSIS MODELING. THE EFFECTS OF RESTRICTED DIFFUSION ON THERMAL REACTION PATHWAYS

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## INTRODUCTION

The technique of model compound immobilization by covalent surface attachment is being employed to investigate the potential impact of restricted diffusional mobility on the thermal reactivity of coal. This restricted mobility may be imposed in coal as a consequence of its cross-linked, macromolecular structure.<sup>1</sup> Thermolysis studies at 350-400 °C of model coal structures covalently attached to a silica surface have shown that significant perturbations in free-radical reaction mechanisms can occur, and result in altered reaction rates and product distributions compared with corresponding fluid phase behavior.<sup>2-4</sup> A detailed study of the thermolysis of surface-immobilized bibenzyl ( $\equiv\text{SiOPhCH}_2\text{CH}_2\text{Ph}$ , represented as  $\sim\text{PhCH}_2\text{CH}_2\text{Ph}$ ) showed that the rate of unimolecular C-C homolysis is similar to that in fluid phases.<sup>2</sup> However, restricted radical and substrate mobility led to the onset of complex free-radical chain pathways on the surface, which produced substantial isomerization, cyclization-dehydrogenation, and hydrodealkylation of bibenzyl moieties. Recent studies have focused on the thermally induced, free radical chain decomposition reactions for surface-immobilized 1,3-diphenylpropane ( $\sim\text{Ph}(\text{CH}_2)_3\text{Ph}$ ,  $\sim\text{DPP}$ )<sup>3</sup> and 1,4-diphenylbutane ( $\sim\text{Ph}(\text{CH}_2)_4\text{Ph}$ ,  $\sim\text{DPB}$ ).<sup>4</sup> For  $\sim\text{DPP}$ , we find that both the reaction rate and product composition are strongly dependent on surface coverage and, hence, the proximity of  $\sim\text{DPP}$  molecules and hydrogen abstracting radicals on the surface. The rates and selectivities of these key bimolecular reaction steps on the surface might also be affected by the structure of neighboring molecules. In the current study, we are beginning to probe this feature by examining the influence of the structure of co-attached aromatic molecules such as biphenyl ( $\sim\text{PhPh}$ ) and diphenylmethane ( $\sim\text{PhCH}_2\text{Ph}$ ) on the reaction rate and regioselectivity in the thermolysis of  $\sim\text{DPP}$ .

## EXPERIMENTAL

Procedures for the synthesis of surface-attached 1,3-diphenylpropane ( $\sim\text{DPP}$ ) by the condensation reaction of  $p\text{-HOPh}(\text{CH}_2)_3\text{Ph}$  (HODPP) with the surface hydroxyls of a high surface area, fumed silica have been fully described elsewhere.<sup>3</sup>  $p\text{-Phenylphenol}$  ( $p\text{-HOPhPh}$ ) was purified by multiple recrystallizations from benzene/hexanes to give a product with GC purity of >99.9%.  $p\text{-Benzylphenol}$  ( $p\text{-HOPhCH}_2\text{Ph}$ ) was first eluted from a silica column with benzene, and then recrystallized two times from benzene/hexanes to give a product with GC purity of >99.9%.

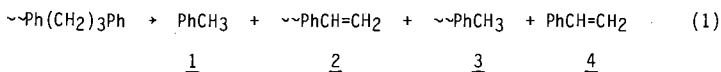
The two-component surfaces were prepared in a manner analogous to that used for preparation of  $\sim\text{DPP}$  with both phenolic components adsorbed onto the surface in a single step prior to the surface attachment reaction. In one case for comparison, a batch of  $\sim\text{DPP}/\sim\text{BP}$  was synthesized in two separate steps. A

saturation coverage batch of  $\sim\sim$ BP was prepared and then reacted with HODPP in a second step to chemically exchange some  $\sim\sim$ DPP molecules with  $\sim\sim$ BP molecules. All surface coverages were analyzed by GC with internal standards following a base hydrolysis procedure that liberates the attached organics as phenols.<sup>3</sup>

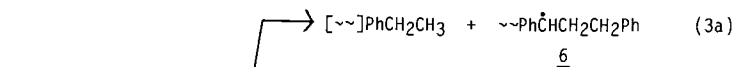
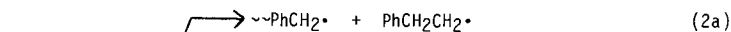
Thermolyses were conducted in sealed, evacuated ( $2 \times 10^{-6}$  torr) T-shaped tubes as described previously.<sup>2,3</sup> Volatile products were collected in a cold trap and analyzed by GC and GC-MS with the use of internal standards. Surface-bound products were removed from the silica by base hydrolysis, and the resulting phenols (or the corresponding trimethylsilyl ether derivatives) were analyzed as above.

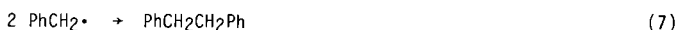
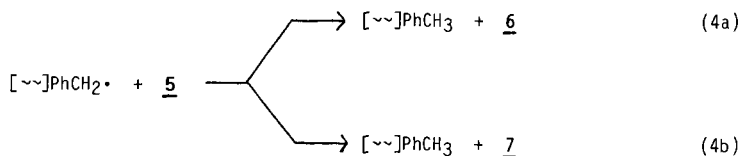
#### RESULTS AND DISCUSSION

Thermolysis of  $\sim\sim$ DPP at 345–400 °C and low conversions produces the four major products shown in Eq. 1 analogous to the cracking reaction observed previously for fluid phase DPP.<sup>5–7</sup> The formation of these products was explained by a



free-radical chain decomposition pathway shown in Eqs. 2–7 with the propagation steps being Eqs. 4–6.<sup>3a</sup> The bracket notation used in Eqs. 3 and 4 indicates that two equations may be written in each case, one with a surface-immobilized species and one with a vapor-phase species.





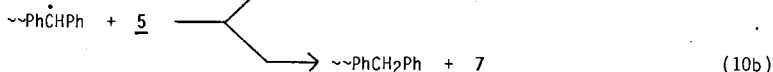
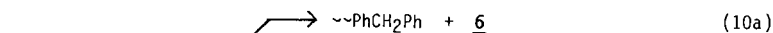
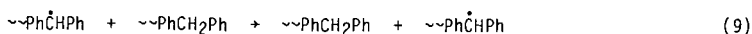
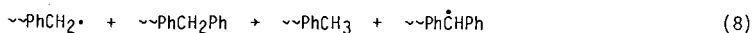
Regioselectivity in the reaction is determined by the relative rates of formation of radicals 6 and 7 by hydrogen abstraction, since the unimolecular  $\beta$ -scission steps (Eqs. 5 and 6) occur very efficiently. We found an increasing selectivity for formation of the product pair 3 and 4 (cycling through radical 7) with increasing  $\sim\sim$ DPP conversion and decreasing initial surface coverage. The surface coverage effect is illustrated at low  $\sim\sim$ DPP conversions in Table 1, which contains new data obtained at a coverage of 0.102 mmol/g. We again use the styrene/toluene yield ratio as the experimental measure of selectivity. Our interpretation is that, at lower coverages, geometrical constraints induced by restricted radical and substrate mobility increasingly favor hydrogen abstraction at the benzylic methylene site farthest from the surface (to favor formation of radical 7) as  $\sim\sim$ DPP molecules become increasingly distant from hydrogen abstracting radicals on the surface. This concept is illustrated in Figure 1.

We also note that the rate of thermolysis of  $\sim\sim$ DPP is more sensitive to changes in surface coverage than fluid phase DPP is to changes in concentration.<sup>5,6</sup> A four-fold decrease in surface coverage resulted in a rate depression by a factor of 17-23.<sup>3a</sup> This result again appears to reflect a substantial sensitivity of bimolecular reaction rates on the surface, such as in Eqs. 3 and 4, to the proximity of  $\sim\sim$ DPP molecules and hydrogen abstracting radicals.

Initial results on the influence of co-attached aromatics on the thermolysis of  $\sim\sim$ DPP are shown in Table 2. Surprisingly, the presence of co-attached biphenyl molecules does not have a major effect on the  $\sim\sim$ DPP thermolysis rate or selectivity compared with corresponding coverages of  $\sim\sim$ DPP alone. This does not appear to be the result of the sample preparation procedure since a  $\sim\sim$ DPP (0.126 mmol/g)/ $\sim\sim$ BP (0.509 mmol/g) batch prepared by a two-step chemical exchange process (see experimental) gave results comparable to those from surfaces prepared by the conventional one-step procedure. The reason for the apparent 2-fold rate acceleration for the  $\sim\sim$ DPP surface in the presence of  $\sim\sim$ BP is under further investigation.

These preliminary data also show that the presence of diphenylmethane molecules has a dramatic effect on the thermolysis of  $\sim\sim$ DPP. Independent control

experiments show that  $\sim\sim\text{DPM}$  alone is thermally stable under the reaction conditions employed (as is  $\sim\sim\text{BP}$ ).<sup>2</sup> In the presence of  $\sim\sim\text{DPM}$ , the rate of  $\sim\sim\text{DPP}$  thermolysis is substantially accelerated (ca. 8-fold increase in conversion) compared with  $\sim\sim\text{DPP}$  alone at comparable coverages, while the product regioselectivity (which is normally  $>1.0$  and increases with larger  $\sim\sim\text{DPP}$  conversions) is essentially eliminated. Our hypothesis at this stage is that bimolecular hydrogen transfer reactions on the surface involving  $\sim\sim\text{DPM}$  are providing a chemical means for "mobilizing" radical centers in an immobilized environment. This radical exchange concept is illustrated in Eqs. 8-10.



This hypothesis of rapid bimolecular hydrogen exchange reactions occurring on the surface is supported by our recent findings that surface-immobilized 1,4-diphenylbutane ( $\sim\sim\text{Ph}(\text{CH}_2)_4\text{Ph}$ ) at high coverages thermally cracks at 400 °C through both benzylic and nonbenzylic radical sites with little selectivity as a consequence of such hydrogen exchange reactions.<sup>4</sup> In the present case, hydrogen transfer steps 8 and 9 could effectively decrease the distance between a radical center and a  $\sim\sim\text{DPP}$  molecule on the surface. This would remove the conformational restrictions leading to the regiospecificity in the reactions that favor formation of 7 over 6, which occur at equivalent  $\sim\sim\text{DPP}$  coverages without  $\sim\sim\text{DPM}$ . By similar arguments, the enhanced  $\sim\sim\text{DPP}$  thermolysis rate could result from an enhanced rate of production of 6 and 7. Research is in progress to further elucidate this interesting reaction chemistry for mixed component surfaces.

#### SUMMARY

Two-component surfaces of surface-attached  $\text{Ph}(\text{CH}_2)_3\text{Ph}$  ( $\sim\sim\text{DPP}$ ) with either  $\text{PhPh}$  ( $\sim\sim\text{BP}$ ) or  $\text{PhCH}_2\text{Ph}$  ( $\sim\sim\text{DPM}$ ) have been prepared, and their thermolysis behavior compared with that of  $\sim\sim\text{DPP}$  alone at comparable surface coverages. In the case of  $\sim\sim\text{DPP}/\sim\sim\text{BP}$  surfaces, no major effects on the  $\sim\sim\text{DPP}$  thermolysis rate or product selectivity were observed. On the other hand, the presence of  $\sim\sim\text{DPM}$  molecules led to a significant acceleration (ca. 8-fold increase in conversion) in the  $\sim\sim\text{DPP}$  thermolysis rate while eliminating the regioselectivity in product formation that was observed previously for  $\sim\sim\text{DPP}$  alone. Our current hypothesis based on this preliminary data is that facile bimolecular hydrogen exchange reactions on the surface involving  $\sim\sim\text{DPM}$  are eliminating conformational restraints on hydrogen abstraction reactions from  $\sim\sim\text{DPP}$  by effectively placing

radicals more proximate to ~DPP molecules on the surface. These results have significant implications for the efficiency with which similar structural features will thermally decay in coal at low temperatures (350-400 °C) by radical chain processes under conditions of restricted diffusion.

#### ACKNOWLEDGMENT

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Table 1. Effect of Surface Coverage on the Selectivity for Thermolysis of  $\sim\sim\text{Ph}(\text{CH}_2)_3\text{Ph}$  at 375 °C.

$\sim\sim\text{DPP}$ Coverage (mmol/g)	$\sim\sim\text{DPP}$ Conversion Range (%)	Selectivity <sup>a</sup>
0.566, 0.586 <sup>b</sup>	2.2 - 4.8	1.00 - 1.03
0.142 <sup>b</sup>	1.5 - 3.1	1.11 - 1.17
0.102	1.0 - 2.8	1.24 - 1.30

<sup>a</sup>Defined as  $\text{PhCH}=\text{CH}_2/\text{PhCH}_3$  yield ratio over the  $\sim\sim\text{DPP}$  conversion range given.

<sup>b</sup>Data from reference 3a.

Table 2. Effect of Co-Attached Aromatics on the Thermolysis of  $\sim\sim\text{Ph}(\text{CH}_2)_3\text{Ph}$ .<sup>a</sup>

Coverage (mmol/g)			$\sim\sim\text{DPP}$ Conversion (%)	Selectivity <sup>c</sup>
$\sim\sim\text{DPP}$	$\sim\sim\text{BPb}$	$\sim\sim\text{DPMb}$		
0.142 <sup>d</sup>	-	-	2.2	1.17
0.142 <sup>d</sup>	-	-	2.2	1.16
0.132 <sup>d</sup>	-	-	2.6	1.17
0.150	0.462	-	4.5	1.15
0.145	0.505	-	5.5	1.11
0.126 <sup>e</sup>	0.509	-	4.6	1.12
0.133	-	0.368	17	0.99
0.133	-	0.368	16	0.99
0.168	-	0.398	19	0.96

<sup>a</sup>Thermolyses were performed at 375 °C for 150 min. <sup>b</sup> $\sim\sim\text{BP}$  and  $\sim\sim\text{DPM}$  are surface-attached biphenyl ( $\sim\sim\text{PhPh}$ ) and diphenylmethane ( $\sim\sim\text{PhCH}_2\text{Ph}$ ), respectively.

<sup>c</sup>Defined as  $\text{PhCH}=\text{CH}_2/\text{PhCH}_3$  yield ratio. <sup>d</sup>Data from reference 3a. <sup>e</sup>Material prepared by a two-step exchange procedure; see text.

Figure 1· Regiospecific Hydrogen Abstraction

